

results support the assumptions used in the derivation of equation 5, i.e., that each electrospray carried approximately the same ion current in the multielectrospray and the liquid flow was distributed approximately equally to each spray emitter. Because of the higher ion current produced by the multielectrosprays, the potential of using multielectrosprays as an ionization source to enhance the sensitivity or dynamic range of mass spectrometry was further evaluated using the arrangement shown in **FIG. 2b**. Sensitivity comparisons between a single electrospray using a fused-silica capillary and multielectrosprays from a microfabricated emitter array were performed using a solution of 50 pg/1L reserpine in 50:50 methanol/water +1% acetic acid introduced at different infusion flow rates. While all the MS parameter settings were held constant, the single electrospray and multielectrosprays sources were interchanged. **FIG. 6a** and **b** shows the SIM mass spectra obtained for single electrospray and three electrosprays for a total sample infusion rate of 1 1L/min. A factor of 2 sensitivity enhancements was achieved using multielectrosprays as the ion source. Similar sensitivity enhancement was also achieved for four electrosprays at a sample flow rate of 2 1L/min compared to the single electrospray, as shown in **FIG. 6c** and **d**. The experimental results are summarized in **FIG. 7** where the number of electrosprays was varied from two to nine at liquid flow rates ranging from 1 to 8 1L/min. For comparison, the results from a single electrospray using a fused-silica capillary are also plotted in **FIG. 7**. A factor of 2-3 sensitivity enhancement was achieved using multielectrosprays at all the sample flow rates evaluated. It was also noted experimentally that stable multielectrospray could be generated at higher liquid flow rates compared to the fused-silica capillary single electrospray.

[0033] The sensitivity enhancements shown in **FIG. 7** are consistent with the theoretical prediction of equation 5 if one assumes that the total electrospray current is the major parameter determining the ion intensity of the mass spectra.

[0034] It is particularly important to understand that the multiemitter ESI source can provide an even greater increase in dynamic range than suggested above. In many (or most) current ESI-MS applications (e.g., using liquid chromatography), much larger sample sizes or liquid flow rates are available than are of present practical utility with ESI. Thus, if all available ESI emitters were to be operated at a flow rate for maximum ion current production, the actual gain in total current would be approximately proportional to the number of emitters. For example, from **FIG. 5a**, the eight-emitter array at 4 1L/min provides an ion current of 0.85 1A; that is more than 8 times greater than the ion current (~0.1 1A) generated from a single capillary at 0.5 1L/min. Thus, a set of eight emitters each operating at 4 1L/min can potentially provide a current of more than 2 1A, much greater than that current achievable by any conventional ESI source used for mass spectrometry.

[0035] Closure

[0036] While a preferred embodiment of the present invention has been shown and described, it will be apparent to those skilled in the art that many changes and modifications may be made without departing from the invention in its broader aspects. For example, while a preferred embodiment utilizing a 3x3 array arranged in a square pattern has been shown and described, it will be apparent to those

having skill in the art that any arrangement of two or more emitters, which may further be arranged in a wide variety of geometrical arrangements, are possible, and will produce the enhanced sensitivity sought by the present invention. The appended claims are therefore intended to cover all such changes and modifications as fall within the true spirit and scope of the invention.

We claim:

1. A method for increasing the total ion current produced from a liquid sample introduced into a mass spectrometer comprising the steps of:

- a. providing an array of spray emitters,
- b. providing said liquid sample in at least one reservoir formed on one side of said array,
- c. interfacing the opposite side of said array with the entrance to a mass spectrometer,
- d. forming an electrospray of said liquid sample at each opposite side of each emitter in said array, and
- e. directing said electrosprays into said entrance of said mass spectrometer.

2. The method of claim 1 wherein said entrance to said mass spectrometer is provided as a multi-capillary inlet.

3. The method of claim 1 wherein said array of spray emitters is provided as fabricated on a single chip.

4. The method of claim 3 wherein said chip is fabricated by a method selected from the group consisting of laser etching, photolithographic patterning, wet chemical etching, laser ablation, plasma etching, casting, injection molding, and hot and cold stamping (embossing).

5. The method of claim 3 wherein said chip is fabricated from materials selected from the group consisting of polycarbonate, polyamide, polymethylmethacrylate, polyoxymethylene, cycloolefin copolymer, polyethylene, polypropylene, polystyrene, plastic, glass, silicon, and combinations thereof.

6. The method of claim 1 wherein said reservoirs are interfaced with a liquid separation device.

7. The method of claim 6 wherein said liquid separation devices are selected from the group consisting of capillary electrophoresis devices, capillary isoelectric focusing devices, micro liquid chromatography, and nano column separation devices

8. The method of claim 1 further comprising the step of enhancing the hydrophobicity of the array by treating the surface with a CF₄ rf plasma.

9. A apparatus for increasing the total ion current produced from a liquid sample introduced into a mass spectrometer comprising:

- a. an array of spray emitters,
- b. at least one reservoir formed on one side of said array, and
- c. a mass spectrometer having an entrance, wherein a liquid sample introduced into at least one of said reservoirs is formed into an electrospray at the opposite side of said array in at least two of said emitters, and said electrospray is then directed into said entrance of said mass spectrometer.

10. The apparatus of claim 9 wherein said entrance to said mass spectrometer is a multi-capillary inlet.